

**United States Patent Application for:**

**HALOGEN-RESISTANT, ANODIZED ALUMINUM FOR USE  
IN SEMICONDUCTOR PROCESSING APPARATUS**

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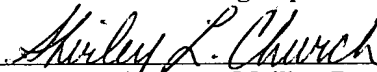
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1 [0001] **HALOGEN-RESISTANT, ANODIZED ALUMINUM FOR USE IN**  
2 **SEMICONDUCTOR PROCESSING APPARATUS**

3  
4 [0002] **BACKGROUND OF THE INVENTION**

5 [0003] 1. Field of the Invention

6 [0004] In general, the present invention relates to a method of fabrication of  
7 semiconductor processing apparatus from an aluminum substrate. In particular, the  
8 invention relates to a structure which provides a particular interface between an  
9 aluminum surface and aluminum oxide overlying that surface. The invention also relates  
10 to a method of producing the interfacial structure.

11 [0005] 2. Brief Description of the Background Art

12 [0006] Semiconductor processing involves a number of different chemical and  
13 physical processes whereby minute integrated circuits are created on a substrate. Layers  
14 of materials which make up the integrated circuit are created by chemical vapor  
15 deposition, physical vapor deposition and epitaxial growth, for example. Some of the  
16 layers of material are patterned using photoresist masks and wet and dry etching  
17 techniques. Patterns are created within layers by the implantation of dopants at particular  
18 locations. The substrate upon which the integrated circuit is created may be silicon,  
19 gallium arsenide, indium phosphide, glass, or any other appropriate material.

20 [0007] Many of the semiconductor processes used to produce integrated circuits  
21 employ halogen or halogen-containing gases or plasmas. Some processes use halogen-  
22 containing liquids. In addition, since the processes used to create the integrated circuits  
23 leave contaminant deposits on the surfaces of the processing apparatus, such deposits are  
24 commonly removed using plasma cleaning techniques which employ at least one  
25 halogen-containing gas. The cleaning procedure may include a wet wipe with deionized  
26 water, followed by a wipe with isopropyl alcohol.

27 [0008] Aluminum has been widely used as a construction material for

1 semiconductor fabrication equipment, at times because of its conductive properties, and  
2 generally because of its ease in fabrication and its availability at a reasonable price.  
3 However, aluminum is susceptible to reaction with halogens such as chlorine, fluorine,  
4 and bromine, to produce, for example,  $\text{AlCl}_3$ ;  $\text{Al}_2\text{Cl}_6$ ;  $\text{AlF}_3$ ; or  $\text{AlBr}_3$ . The aluminum-  
5 fluorine compounds can flake off the surfaces of process apparatus parts, causing an  
6 eroding away of the parts themselves, and serving as a source of particulate  
7 contamination of the process chamber (and parts produced in the chamber). Many of the  
8 compounds containing aluminum and chlorine and many of the compounds containing  
9 aluminum and bromine are volatile and produce gases under semiconductor processing  
10 conditions, which gases leave the aluminum substrate. This creates voids in the structure  
11 which render the structure unstable and produce a surface having questionable integrity.

12 [0009] A preferred means of protecting the aluminum surfaces within process  
13 apparatus has been an anodized alumina coating. Anodizing is typically an electrolytic  
14 oxidation process that produces an integral coating of relatively porous aluminum oxide  
15 on the aluminum surface. Despite the use of anodized alumina protective layers, the  
16 lifetime of anodized aluminum parts in semiconductor processing apparatus, such as  
17 susceptors in CVD reactor chambers, and gas distribution plates for etch process  
18 chambers has been limited, due to the gradual degradation of the protective anodized  
19 film. Failure of the protective anodized film leads to excessive particulate generation  
20 within the reactor chamber, requiring maintenance downtime for replacing the failed  
21 aluminum parts and for cleaning particulates from the rest of the chamber.

22 [0010] Miyashita et al., in U.S. Patent No. 5,039,388, issued August 13, 1991,  
23 describe a plasma forming electrode used in pairs in a semiconductor processing  
24 chamber. The electrode is formed from a high purity aluminum or an aluminum alloy  
25 having a chromic acid anodic film on the electrode surface. The chromic acid anodized  
26 surface is said to greatly improve durability when used in a plasma treatment process in  
27 the presence of fluorine-containing gas. The electrode is described as formed from a

1 high purity aluminum such as JIS 1050, 1100, 3003, 5052, 5053, and 6061 or similar  
2 alloys such as Ag-Mg alloys containing 2 to 6 % by weight magnesium.  
3 [0011] U.S. Patent No. 5,756,222 to Bercaw et al., issued May 26, 1998, and titled:  
4 "Corrosion-Resistant Aluminum Article For Semiconductor Processing Equipment",  
5 describes an article of manufacture useful in semiconductor processing which includes a  
6 body formed from a high purity aluminum-magnesium alloy having a magnesium  
7 content of about 0.1 % to about 1.5% by weight, either throughout the entire article or at  
8 least in the surface region which is to be rendered corrosion-resistant, and a mobile  
9 impurity atom content of less than 0.2 % by weight. Mobile impurity atoms are said to  
10 consist of metal atoms other than magnesium, transitional metals, semiconductors, and  
11 atoms which form semiconductor compounds. Mobile impurity atoms particularly  
12 named include silicon, iron, copper, chromium and zinc. The high purity aluminum-  
13 magnesium alloy may be overlaid by a cohesive film which is permeable to fluorine, but  
14 substantially impermeable to oxygen. Examples of such a film include aluminum oxide  
15 or aluminum nitride. The subject matter disclosed in this patent is hereby incorporated  
16 by reference in its entirety.

17 [0012] U.S. Patent No. 5,811,195 to Bercaw et al., issued September 22, 1998,  
18 and titled: "Corrosion-Resistant Aluminum Article For Semiconductor Equipment",  
19 further discloses that the magnesium content of the aluminum article may be in the range  
20 of about 0.1% to about 6.0% by weight of the aluminum article. However, for  
21 operational temperatures of the article which are greater than about 250 °C, the  
22 magnesium content of the aluminum article should range between about 0.1 % by weight  
23 and about 1.5 % by weight of the article. In addition, an article is described in which the  
24 mobile impurities other than magnesium may be as high as about 2.0 % by weight in  
25 particular instances. One example is when there is a film overlying the exterior region of  
26 the article body, where the film comprises aluminum oxide or aluminum. Another  
27 example is where there is a magnesium halide layer having a thickness of at least about

1 0.0025 microns over the exterior surface of the aluminum article. The subject matter  
2 disclosed in this patent is hereby incorporated by reference in its entirety.

3 [0013] For an aluminum alloy to be useful in the fabrication of semiconductor  
4 processing apparatus, it must not only exhibit the desired magnesium content and low  
5 level of mobile impurity atoms, but it must also have desirable mechanical properties.  
6 The mechanical properties must enable machining to provide an article having the  
7 desired dimensions. For example, if the alloy is too soft, it is difficult to drill a hole, as  
8 material tends to stick during the drilling rather than to be removed by the drill.

9 Controlling the dimensions of the machined article is more difficult. There is a penalty  
10 in machining cost. In addition, the mechanical properties of the article affect the ability  
11 of the article to perform under vacuum. For example, a process chamber must exhibit  
12 sufficient structural rigidity and resistance to deformation that it can be properly sealed  
13 against high vacuum. Finally, the mobile impurities need to be uniformly distributed  
14 throughout the article so that there is a uniform transfer of loads and stresses.

15 [0014] The "Metals Handbook, Ninth Edition", Volume 2, copyright 1979 by the  
16 American Society for Metals, describes the heat treatment of aluminum alloys beginning  
17 at Page 28. In particular, for both heat treatable and non-heat-treatable aluminum alloys,  
18 annealing to remove the effects of cold work is accomplished by heating within a  
19 temperature range from about 300 °C (for batch treatment) to about 450 °C (for  
20 continuous treatment). The term "heat treatment" applied to aluminum alloys is said to  
21 be frequently restricted to the specific operations employed to increase strength and  
22 hardness of the precipitation-hardenable wrought and cast alloys. These are referred to  
23 as "heat-treatable" alloys, to distinguish them from alloys in which no significant  
24 strengthening can be achieved by heating and cooling. The latter are generally said to be  
25 referred to as "non-heat-treatable" alloys, which, in wrought form, depend primarily on  
26 cold work to increase strength. At Page 29, Table 1 provides typical full annealing  
27 treatments for some common wrought aluminum alloys. The 5xxx series of alloys are

1 considered to be “non-heat-treatable” aluminum alloys and are annealed at about 345 °C.  
2 The 5xxx series of aluminum alloys are of interest for use in fabricating semiconductor  
3 processing apparatus because some of the alloys offer mobile impurity concentrations  
4 within acceptably moderate ranges, while providing sufficient magnesium content to  
5 perform in the manner described in the Bercaw et al. patents.

6 [0015] Standard thermal stress relief of “non-heat-treatable” aluminum alloys  
7 such as the 5xxx series assumes peak temperatures approaching 345 °C and generic ramp  
8 rates and dwell times, without regard to the alloy or the final use of individual articles  
9 fabricated from the alloy. Aluminum alloys begin to exhibit grain growth at  
10 temperatures approaching 345 °C, and enhanced precipitation of non-aluminum metals  
11 at the grain boundaries, which may lead to cracking along the grain boundaries during  
12 machining. The above factors also reduce the mechanical properties of the alloy, by  
13 affecting the uniformity of the alloy composition within the article.

14 [0016] When the article fabricated from an aluminum alloy is to be used in a  
15 corrosive atmosphere, it frequently necessary to provide a protective coating such as  
16 anodized aluminum over the aluminum surface. This is particularly true for applications  
17 of aluminum in semiconductor processing where corrosive chlorine or fluorine-  
18 containing etchant gases and plasmas generated from these gases are employed. A stable  
19 aluminum oxide layer over the aluminum alloy surface can provide chemical stability  
20 and physical integrity which is effective in protecting the aluminum alloy surface from  
21 undergoing progressive erosion/corrosion. As described in the Bercaw et al. patents, the  
22 presence of an aluminum oxide layer over the surface of the specialty magnesium-  
23 containing aluminum alloy described therein helps maintain a magnesium halide  
24 protective component at or near the surface of the aluminum alloy. The aluminum oxide  
25 helps prevent abrasion of the relatively soft magnesium halide component. The  
26 combination of the aluminum oxide film and the magnesium halide protective  
27 component overlying the specialty aluminum alloy provides an article capable of long

1 term functionality in the corrosive environment. However, one requirement which has  
2 not been adequately addressed in the past is the mechanical performance of the article.  
3 In attempting to obtain the mechanical properties required for the aluminum alloy body  
4 of the article, it is possible to affect the surface of the aluminum alloy in a manner such  
5 that a subsequently-formed aluminum oxide (anodized) layer does not form a proper  
6 interface with the aluminum alloy, especially at the grain boundary areas. This creates  
7 gaps between the aluminum oxide layer and the underlying aluminum surface. This  
8 porosity promotes a breakdown in the protective aluminum oxide layer, which leads to  
9 particle formation, and may cause a constantly accelerating degradation of the protective  
10 aluminum oxide film.

11 [0017] Not only is there significant expense in equipment maintenance and  
12 apparatus replacement costs due to degradation of the protective aluminum oxide film,  
13 but if a susceptor, for example, develops significant surface defects, these defects can  
14 translate through a silicon wafer atop the susceptor, creating device current leakage  
15 or even short. The loss of all the devices on a wafer can be at a cost as high as \$50,000  
16 to \$60,000 or more.

17 [0018] It is clear that there are significant advantages to providing an interface  
18 between a protective aluminum oxide and the underlying aluminum alloy with sufficient  
19 stable mechanical, chemical, and physical properties to extend the lifetime of the  
20 protective film. It is also clear that it would be beneficial to provide a less porous, dense,  
21 and more stable aluminum oxide film.

22 [0019] **SUMMARY OF THE INVENTION**

23 [0020] We have discovered that the formation of particulate inclusions at the  
24 surface of an aluminum alloy article, which inclusions interfere with a smooth transition  
25 from the alloy surface to an overlying aluminum oxide protective film, can be controlled  
26 by a combination of processing parameters which include: maintaining the content of

1 mobile impurities within a specific range; heat-treating the aluminum alloy at a  
2 temperature less than about 330 °C , while employing temperature ramp rates and dwell  
3 times specific to the aluminum alloy composition and the size and shape of the article;  
4 and, creating the aluminum oxide protective film by employing a particular electrolytic  
5 process. When these factors are taken into consideration, an improved aluminum oxide  
6 protective film is obtained, and the protective lifetime of the film is significantly  
7 extended compared with the lifetime of previously known protective anodized films.

8 [0021] In particular, the aluminum alloy which is used to form the body of an  
9 article of apparatus, may be forged, extruded or rolled. The aluminum alloy should have  
10 the following composition by weight %: a magnesium concentration ranging from  
11 about 3.5 % to about 4.0 %, a silicon concentration ranging from 0 % to about 0.03 %, an  
12 iron concentration ranging from 0% to about 0.03 %, a copper concentration ranging  
13 from about 0.02 % to about 0.07 %, a manganese concentration ranging from about  
14 0.005 % to about 0.015 %, a zinc concentration ranging from about 0.08 % to about 0.16  
15 %, a chromium concentration ranging from about 0.02 % to about 0.07%, and a titanium  
16 concentration ranging from 0% to about 0.01 %, with other single impurities not  
17 exceeding about 0.03 % each and other total impurities not exceeding about 0.1 %.

18 [0022] In addition, the aluminum alloy is required to meet a particular  
19 specification with respect to particulates formed from mobile impurities. Of the  
20 particulate agglomerations of impurity compounds, at least 95 % of all particles must be  
21 less than 5  $\mu\text{m}$  in size . Five (5) % of the particles may range from 5  $\mu\text{m}$  to 20  $\mu\text{m}$  in  
22 size. Finally, no more than 0.1 % of the particles may be larger than 20  $\mu\text{m}$ , with no  
23 particles being larger than 40  $\mu\text{m}$ .

24 [0023] The aluminum alloy described above is referred to as LP<sup>TM</sup> alloy herein.  
25 LP<sup>TM</sup> is a trademark of Applied Materials, Inc. of Santa Clara, California.

26 [0024] The LP<sup>TM</sup> aluminum alloy in sheet or extruded or forged form, or after pre-  
27 machining into a desired shape, is typically stress relieved at a temperature of about 330



1 °C or less, prior to creation of an aluminum oxide protective film over the article surface.  
2 This stress relief provides a more stable surface for application of the aluminum oxide  
3 protective film. A side benefit of the heat treatment process is that it provides additional  
4 hardening of the alloy, despite prior art assertions to the contrary. When the LP<sup>TM</sup>  
5 aluminum alloy article is machined from a block of material, it is advantageous to stress  
6 relieve the block of material after machining, to relieve stress resulting from the  
7 machining operation. We have discovered that it is very important to heat relieve  
8 thermal stress in the LP<sup>TM</sup> aluminum alloy using lower peak temperatures than  
9 commonly recommended for aluminum alloys. Employment of a peak stress relief  
10 temperature of less than about 330°C will minimize the undesirable precipitation of  
11 impurities at the aluminum grain boundaries and eliminate unwanted aluminum  
12 grain growth. This ensures the desired material properties of the alloy with respect to  
13 grain structure, non-aluminum metal (mobile impurity) distribution and mechanical  
14 properties in the article produced. By controlling the grain size of the aluminum alloy,  
15 the distribution of mobile impurities within the alloy, and the residual stress within the  
16 article to be anodized, the interface between a protective aluminum oxide film and the  
17 underlying aluminum alloy provides a uniform transition from one crystal structure to  
18 another, improving the performance and lifetime of the article.

19 [0025] The aluminum oxide protective film is applied using an electrolytic  
20 oxidation process which produces an integrated coating of aluminum oxide which is  
21 porous to halogens but not to oxygen. Typically, the article to be anodized is immersed  
22 as the anode in an acid electrolyte, and a DC current is applied. On the surface, the  
23 aluminum alloy is electrochemically converted into a layer of aluminum oxide.

24 [0026] Prior to the anodization process, it is important to chemically clean and  
25 polish the aluminum alloy surface. The cleaning is carried out by contacting the surface  
26 of the aluminum article with an acidic solution including about 60 % to 90 % technical  
27 grade phosphoric acid, having a specific gravity of about 1.7 and about 1% - 3 % by

1 weight of nitric acid. The article temperature during cleaning is typically in the range  
2 of about 100°C, and the time period the surface of the article is in contact with the  
3 cleaning solution ranges from about 30 to about 120 seconds. This cleaning and  
4 polishing time period is often referred to as the “bright dip” time. Typically the  
5 cleaning process is followed by a deionized water rinse.

6 [0027] Subsequent to cleaning, anodization of the aluminum alloy surface is  
7 carried out, to create a protective aluminum oxide film on the alloy surface. The  
8 anodization is carried out electrolytically in a water-based solution comprising 10 % to  
9 20 % by weight sulfuric acid and about 0.5 % to 3.0 % by weight oxalic acid. The  
10 anodizing temperature is set within a range from about 5 °C to about 25 °C, and  
11 typically within a range from about 7 °C to about 21 °C . The article to be “anodized”  
12 serves as the anode, while an aluminum sheet of standard 6061 serves as the cathode.  
13 We have discovered that it is very important that during the electrolytic oxidation  
14 process the current density, in Amps / Square Foot (ASF) in the electrolytic bath, ranges  
15 from about 5 ASF to less than 36 ASF. Further, the “barrier layer” thickness (shown  
16 as 310 on Figure 3C) at the base of the aluminum oxide film is controlled by the  
17 operating (anodization) voltage, which typically ranges from about 15 V to about 30 V.  
18 Common practice has indicated that each 1V increase in anodization voltage increases  
19 the barrier layer thickness at the base of the film by about 14 Å.

20 [0028] The particular combination of process variables described above also  
21 produces an oxidized aluminum layer which is more densely packed and more uniform  
22 than previously known in the art. For example, the size of the internal pores (shown as  
23 314 on Figure 3C) within the hexagonal cells of the oxidized aluminum film of the  
24 present invention range in size from about 300 Å to about 700 Å. This is compared with  
25 previously known oxidized aluminum films, where the pore size varied from about 100  
26 Å to about 2000 Å in diameter. As a result, the density of the present oxidized film is  
27 generally higher, providing improved abrasion resistance. Depending on the application,

1 the normal range of the anodized film thickness ranges between about 0.7 mils to about  
2 2.5 mils (18  $\mu\text{m}$  to 63 $\mu\text{m}$ ).

3 [0029] Although the above anodization process is beneficial for any article formed  
4 from the specialized halogen-resistant aluminum alloy article described in the Bercaw et  
5 al. patents, it is particularly beneficial when the aluminum alloy is LP<sup>TM</sup>. In addition,  
6 when the halogen-resistant aluminum article is heat treated for stress relief and hardening  
7 at a temperature of less than about 330 °C, the performance lifetime of the anodized  
8 semiconductor apparatus is further improved. The best-performing anodized aluminum  
9 alloy article is one formed from LP<sup>TM</sup> alloy which has been heat treated at temperatures  
10 below about 330 °C, and which has an electrochemically applied aluminum oxide  
11 protective film. The quality of the protective coating is further improved when the alloy  
12 article surface is cleaned prior to anodization, as previously described.

13 [0030] **BRIEF DESCRIPTION OF THE DRAWINGS**

14 [0031] A better understanding of the invention is obtained when the following  
15 detailed description is considered in conjunction with the following drawings in which:

16 [0032] Figure 1 illustrates a schematic three-dimensional structure 100 of an  
17 aluminum alloy 102 having an aluminum oxide (anodized) film 104 on its upper surface  
18 106, where there are defects (particulate inclusions 108) at the interface between the  
19 alloy surface 106 and the bottom of the anodized film surface 109, which cause the  
20 formation of conduits 116 which leave the aluminum alloy surface 106 open to attack by  
21 reactive species.

22 [0033] Figure 2A shows a schematic three-dimensional structure 200 of an  
23 aluminum alloy 202 having an upper surface 205 comprised of aluminum crystalline  
24 grains 204.

1 [0034] Figure 2B shows the upper surface 205 of the structure 200 in more detail,  
2 where aluminum grains 204 have boundaries 206 with particulate inclusions 208 present  
3 within boundaries 206.

4 [0035] Figure 3A shows a schematic three-dimensional view of a structure 300  
5 which is an aluminum alloy 302 , where the upper surface 306 includes aluminum  
6 crystalline grains 304 and particulate inclusions which are small in size 308a and large  
7 in size 308b.

8 [0036] Figure 3B shows a schematic three-dimensional view of a structure 320  
9 after formation of an anodized layer (aluminum oxide film) 304 over the upper surface  
10 306 of aluminum alloy 302. Large particulates 308b have caused the formation of  
11 conduits 316 from the upper surface 305 of anodized layer 304, through to the upper  
12 surface 306 of aluminum alloy 302.

13 [0037] Figure 3C shows a schematic three-dimensional view of a structure 330  
14 after formation of an anodized layer 304 over the upper surface 306 of aluminum alloy  
15 302. However, only small particulates 308a are present at the upper surface 306 of  
16 aluminum alloy 302, and no conduits are present from the upper surface 305 of anodized  
17 layer 304 to the upper surface 306 of aluminum alloy 302.

18 [0038] **DETAILED DESCRIPTION OF THE INVENTION**

1 [0039] As a preface to the detailed description, it should be noted that, as used in  
2 this specification and the appended claims, the singular forms “a”, “an”, and “the”  
3 include plural referents, unless the context clearly dictates otherwise.

4 [0040] The objective of the present invention is to provide a semiconductor  
5 processing apparatus which is resistant to corrosive processing conditions. In general,

1 the body of the apparatus is formed from an aluminum alloy. To enable the aluminum  
2 alloy to resist corrosion, an aluminum oxide protective film is applied over a surface of  
3 the aluminum alloy which is to be exposed to the corrosive processing environment. To  
4 obtain the best corrosion resistance and longest acceptable performance lifetime for the  
5 apparatus article, the article is fabricated in a particular manner. As described above, for  
6 best results, the aluminum alloy used for the body of the article should be formed from a  
7 specialized halogen-resistant aluminum alloy of the kind described in the Bercaw et al.  
8 patents. It is particularly beneficial when the aluminum alloy is the LP<sup>TM</sup> alloy. In  
9 addition, it is advantageous to heat treat the aluminum alloy for stress relief and  
10 hardening at a temperature of less than about 330 °C prior to creation of the protective  
11 aluminum oxide film over a surface of the apparatus article. The aluminum oxide film is  
12 then applied using the electrolytic anodization process described below in detail. A  
13 semiconductor processing apparatus article formed from LP<sup>TM</sup> alloy, where the alloy  
14 was heat treated at a temperature below about 330 °C to relieve stress while reducing the  
15 possibility of an increase in the size of particulates formed at aluminum grain boundaries  
16 during the heat treatment, and where an electrochemically applied aluminum oxide  
17 protective film applied using the method described herein performs particularly well.

18 [0041] For particular applications, the high purity alloy specification related to  
19 particle size and particle size distribution may be relaxed from the requirement that no  
20 more than 0.1 % of the particles may be larger than 20  $\mu\text{m}$ , with no particles being larger  
21 than 40  $\mu\text{m}$  to a requirement that no more than 0.2 % of the particles may be larger than  
22 20  $\mu\text{m}$ , with no particles being larger than 50  $\mu\text{m}$ .

23 [0042] With reference to Figure 1, a structure 100 is illustrated, the structure  
24 comprising an aluminum alloy 102 and an anodized aluminum layer 104 created by an  
25 electrolytic oxidation process. The anodized aluminum layer (film) 104 consists of a  
26 fairly dense  $\text{Al}_2\text{O}_3$  barrier layer having a thickness ranging between about 100 Å and  
27 about 2000 Å. The anodized film 104 grows in the form of hexagonal cells 112 with

1 internal pores 114 which are typically about 100 Å to about 2000 Å in diameter,  
2 depending on the conditions of anodization. Thus, the principal protection of base  
3 aluminum alloy 102 from the harsh halide-enriched plasma environment in a CVD  
4 reactor chamber, for example, is dense barrier layer 110 at the base of anodized film 104,  
5 and a magnesium halide film (not shown) formed on the upper surface 106 of aluminum  
6 alloy 102 due to the presence of magnesium in aluminum alloy 102. The hexagonal cells  
7 112 contribute to increased wear resistance of the anodized aluminum layer 102.

8 However, halogen atoms, ions, and activated species are relatively small in size, with  
9 fluorine ions being less than about 5 Å in diameter, for example. It has been determined  
10 that there is a high probability of penetration of the anodized aluminum film by about 5  
11 % - 10 % of the active fluorine ions present in a gaseous fluorine-containing plasma.

12 The magnesium halide film (not shown) is typically only about 25 Å thick, so it is  
13 desirable to have the anodized film 104 be densely formed with minimal pore 114  
14 diameter and to have the lower surface 109 of anodized film 104 interface tightly with  
15 the upper surface 106 of aluminum alloy 102.

16 [0043] Mobile impurities within the aluminum alloy form agglomerations within  
17 the alloy which tend to migrate to the upper surface 106 of alloy 102. The agglomerated  
18 impurities, which are typically comprised of magnesium, silicon, iron, copper,  
19 manganese, zinc, chromium, titanium, and compounds thereof, may appear as  
20 particulates 108 at aluminum grain boundaries. If the particulates 108 are sufficiently  
21 large, they prevent a good interface from forming between the newly growing aluminum  
22 oxide film 104 at its base 110 and the upper surface 106 of aluminum alloy 102. The  
23 presence of particulates 108 may cause the formation of gaps, voids, or microcracks,  
24 which create conduits 116 through the thickness of aluminum oxide film 104. The gaps  
25 or voids may form beneath a pore 114 which also creates conduits through the thickness  
26 of aluminum oxide film 104. These gaps, voids and microcracks open a pathway  
27 through the aluminum oxide film 104 which exposes the upper surface 106 of aluminum

1 alloy 102 to attack by reactive species.

2 [0044] Figure 2A shows a schematic three-dimensional view of a structure 200  
3 which includes an aluminum alloy layer 202, illustrating grains 204 at the upper surface  
4 205 of aluminum alloy layer 202. Figure 2B shows an enlargement of the upper surface  
5 205 of aluminum alloy layer 202, illustrating aluminum grains 204, grain boundaries  
6 206, and mobile impurity agglomerates in the form of particulates 208a and 208b. The  
7 208a particulates are small in size, typically less than about 5  $\mu\text{m}$ . The 208b particulates  
8 are much larger in size, typically larger than about 20  $\mu\text{m}$ .

9 [0045] Figure 3A shows a schematic three-dimensional view of a structure 300  
10 which includes an aluminum alloy layer 302, illustrating grains 304 at the upper surface  
11 305 of aluminum alloy layer 302. Mobile impurity agglomerates are present in the form  
12 of large particulates 308 b and small particulates 308a.

13 [0046] Figure 3B shows a structure 320 which illustrates the effect of the presence  
14 of the large particulates 308b on an aluminum oxide film 304 formed over large  
15 particulates 308b. Conduits 316 are formed from upper surface 305 through to  
16 underlying aluminum alloy layer 302, due in part to structural differences between the  
17 mobile impurity compounds making up the large particulates and the aluminum grain  
18 structure. For example, the aluminum grain structure is face-centered-cubic (fcc), which  
19 has a space group  $\text{Fm}\bar{3}\text{m}$  ( $\text{O}_\text{h}^5$ ), and Lattice Parameter (A) where  $a = 4.050$ . This  
20 compares with mobile impurity compounds such as, for example:  $\text{Mg}_2\text{Al}_3$  having an fcc  
21 structure type, a space group  $\text{Fd}\bar{3}\text{m}$  ( $\text{O}_\text{h}^7$ ), and Lattice Parameter (A), where  $a = 28.160$  ;  
22  $\text{FeAl}_3$  having a mono structure type, a space group  $\text{C}2/\text{m}(\text{C}_{2\text{h}}^3)$ , and Lattice Parameter  
23 (A), where  $a = 15.490$ ,  $b = 8.080$ ,  $c = 12.480$ , and  $\beta = 107^\circ 43'$  ;  $\text{FeSiAl}_5$  having a mono  
24 structure type, a space group  $\text{C}2/\text{m}(\text{C}_{2\text{h}}^3)$ , and Lattice Parameter (A), where  $a = 6.120$ ,  $b =$   
25  $6.120$ ,  $c = 41.480$ , and  $\beta = 91^\circ$  ;  $\text{CrAl}_7$ , having an ortho structure type and a Lattice  
26 Parameter (A), where  $a = 24.800$ ,  $b = 24.700$ , and  $c = 30.200$  ;  $\text{MnAl}_4$  having a space  
27 group  $\text{Pnnn}$  and a Lattice Parameter (a), where  $a = 6.795$ ,  $b = 9.343$ , and  $c = 13.839$  ; and

1 Cr<sub>2</sub>Mg<sub>3</sub>Al having an fcc structure type, a space group Fd3m (O<sub>h</sub><sup>7</sup>), and Lattice Parameter  
2 (A), where a = 14.550. This illustrates the importance of minimizing the quantity of  
3 mobile impurity atoms which are available to react with aluminum to form compounds  
4 which agglomerate to form large particulates 308b at the grain boundaries of aluminum  
5 grains 304. A comparison of the differences between the structural characteristics of  
6 aluminum and such mobile impurity compounds also indicates why the presence of such  
7 mobile impurity compounds creates stress within the aluminum alloy and affects  
8 mechanical properties of the alloy as well.

9 [0047] Figure 3C shows a structure 330 which illustrates that the presence of  
10 small particulates 308a does not disrupt the interface between the upper surface 306 of  
11 aluminum alloy 302 and the lower surface 309 of aluminum oxide layer 304 to the extent  
12 that porosity through aluminum oxide layer 304 is increased. The upper surface of  
13 aluminum oxide layer 305 is essentially undisturbed, and the lower dense portion 310 of  
14 aluminum oxide layer 310 is generally undisturbed.

15 [0048] We were able to control two major factors which affect the size and  
16 distribution of the particulates 308. The two factors were the amount of mobile  
17 impurities in the LP<sup>TM</sup> aluminum alloy as originally formed, and the heat treatment  
18 process used for reducing stress and hardening the LP<sup>TM</sup> aluminum alloy prior to creation  
19 of the aluminum oxide layer 304.

20 [0049] With respect to the LP<sup>TM</sup> aluminum alloy, the composition of the aluminum  
21 alloy is high purity, with mobile impurities limited so that the following weight % of  
22 such mobile impurities are present: magnesium at a magnesium concentration ranging  
23 from about 3.5 % to about 4.0 %, a silicon concentration ranging from 0 % to about 0.03  
24 %, an iron concentration ranging from 0% to about 0.03 %, a copper concentration  
25 ranging from about 0.02 % to about 0.07 %, a manganese concentration ranging from  
26 about 0.005 % to about 0.015 %, a zinc concentration ranging from about 0.08 % to  
27 about 0.16 %, a chromium concentration ranging from about 0.02 % to about 0.07%, and



1 a titanium concentration ranging from 0% to about 0.010 %, with other single impurities  
2 not exceeding about 0.03 % each and other total impurities not exceeding about 0.1 %.

3 The alloy composition measurement was made by Sparking method for GDMS or by  
4 Molten method for GDMS.

5 [0050] In addition to the compositional limitations, applicants required the  
6 following additional specifications with respect to the LP<sup>TM</sup> aluminum alloy. Of the  
7 particulate agglomerations of impurity compounds, at least 95 % of all particles must be  
8 less than 5  $\mu\text{m}$  in size . Five (5) % of the particles may be larger than 5  $\mu\text{m}$  but less than  
9 20  $\mu\text{m}$  in maximum dimension. Finally, no more than 0.1 % of the particles may be  
10 larger than 20  $\mu\text{m}$ , with no particles being larger than 40  $\mu\text{m}$ . The analysis technique  
11 used to determine particle size and size distribution was based on back scattered image  
12 analysis under the scanning electron microscope (SEM). The equipment used to conduct  
13 measurements was a KLA TENCOR® Surf Scan machine. The magnification was at  
14 500x in order to assess the constituent particles. The area of each image was about 150  
15  $\mu\text{m}$  x 200  $\mu\text{m}$ . The digital resolution was at least 0.2  $\mu\text{m}$ /pixel. At least 40 images were  
16 taken at random from a sample area of 0.75 inch diameter in order to obtain good  
17 assessment of various areas on the metal microstructure, to ensure meaningful statistical  
18 analysis. The back scattered images were digitally stored to provide for statistical  
19 analysis. The images were transferred to an image analyzer and the distribution of the  
20 particles with a mean atomic number higher than that of Al (white in the images) were  
21 detected and measured. The digital resolution allowed for measurement of particles as  
22 small as 0.2  $\mu\text{m}$ . The image analyzer used was IBAS by Zeiss. Particle agglomerates  
23 were seen as precipitated particles. The parameters to determine the particle's size  
24 distribution were: the diameter of the area equal circle  $\phi = 2 \times \text{square root of } (A/\pi)$ ,  
25 where A is the area of a particle. The class limits were as follows: 0.2; 1; 2; 3; 4; 5; 20;  
26 40. The number of particles in each class was determined and then normalized to 100 %  
27 for the total number of particles measured.

1 [0051] Cabot Corporation has offered a high purity aluminum alloy designated C-  
2 276 for general sale for more than 20 years. This high purity aluminum alloy is similar  
3 in chemical composition to the high purity aluminum alloy we have developed for use in  
4 the present invention. However, the C-276 alloy compositional ranges exceed the  
5 maximum concentration specified for particular mobile impurities in the present  
6 invention, with respect to copper, manganese, chromium and zinc. The difference in  
7 copper concentration is important, as copper migration within semiconductor processing  
8 equipment is a problem. In addition, published data for the C276 alloy indicates that  
9 approximately 3 % to 4 % of the particles present in extruded C-276 are 20  $\mu\text{m}$  or larger  
10 in size. No maximum particle size is specified. This is likely to present a surface prior  
11 to anodization which will cause problems in terms of creating voids, gaps or cracks in an  
12 anodized film formed over such a surface. On machining of this surface prior to  
13 anodization, the 3 % to 4 % of large particles will present localized microcracking and  
14 loosely bonded particulates. Since a typical aluminum oxide protective film is about 25  
15  $\mu\text{m}$  thick, there is a possibility that particulates on the C-276 aluminum alloy surface  
16 may pass all the way through the anodized film. For purposes of comparison, the LP<sup>TM</sup>  
17 extruded alloy contains less than 0.1 % of particles having a size of 20 $\mu\text{m}$  or larger.

18 [0052] We also controlled the heat-treatment temperature of the LP<sup>TM</sup> alloy during  
19 stress relief and hardening, so that particulate inclusions would not be increased in size  
20 during the heat-treatment process. The heat treatment temperature during stress relief  
21 and hardening was maintained at 330 °C or lower. To determine the effect of heat  
22 treatment on the size and number of impurity compound particulate inclusions, the test  
23 described above may be carried out before and after the heat treatment process. The heat  
24 treatment process may be adjusted if necessary. As previously mentioned, typically the  
25 heat treatment for stress relief and hardening is performed prior to the creation of the  
26 aluminum oxide protective film over a surface of the aluminum alloy.

27 [0053] After preparation of the LP<sup>TM</sup> high purity aluminum alloy article (typically

1 including heat treatment for stress relief and hardening), the surface of the article which  
2 was to be anodized was cleaned (and chemically polished). The cleaning was carried out  
3 by immersing the aluminum article in an acidic solution including about 60 % to 90 %  
4 by weight of technical grade phosphoric acid, having a specific gravity of about 1.7, and  
5 about 1% - 3 % by weight of nitric acid. The article temperature during cleaning was in  
6 the range of about 100 °C, and the article was in the cleaning solution for a time period  
7 ranging from about 30 to about 120 seconds. This cleaning and polishing time period,  
8 which is typically referred to as the “bright dip” time, is particularly important. If the  
9 cleaning time is too short, contaminants may remain on the article surface. If the  
10 cleaning time is too long, craze lines appear in the subsequently formed aluminum  
11 oxide film and the film degrades more rapidly during the lifetime of the article. In  
12 addition customers for the corrosion resistant semiconductor processing apparatus who  
13 observe the microcracks worry about what is happening beneath the microcracks.  
14 Typically, the cleaning process was followed by a deionized water rinse.

15 [0054] The aluminum oxide protective film was generated using an electrolytic  
16 oxidation process which produced an integrated structure including a protective film of  
17 aluminum oxide which exhibited improved corrosion resistance. The article to be  
18 anodized was immersed as the anode in an electrolyte bath comprised of a water-based  
19 solution including 10 % to 20 % by weight sulfuric acid and about 0.5 % to 3.0 % by  
20 weight of oxalic acid. The anodizing temperature was set within a range from about 7  
21 °C to about 21 °C . The article served as the anode, while a sheet of 6061 aluminum  
22 served as the cathode. A DC current was applied to the electrolytic circuit, taking care  
23 that the current density, in Amps / Square Foot (ASF) in the electrolytic bath, ranged  
24 from 5 ASF to less than 36 ASF. The current density is particularly important, since a  
25 current density of less than 5 ASF will not produce a sufficiently dense aluminum oxide  
26 protective film and a current density greater than 36 ASF produces a film which degrades  
27 during its lifetime, including localized burning, especially at sharp edged areas.

1 [0055] The particular combination of process variables, including the use of LP™  
2 alloy, heat treating at less than 330 °C, and the creation of a protective aluminum oxide  
3 film using the anodization process described above, generated a structure which included  
4 a more dense and uniform aluminum oxide film than that previously obtained. Data for  
5 anodized films in general indicated that the internal pores within the hexagonal  
6 aluminum oxide cells ranged in size from about 100 Å to about 2,000Å. Data for the  
7 anodized film produced by our method indicates the internal pores range from about 300  
8 Å to about 750 Å, falling within the bottom 30 % of the general range. As a result, the  
9 anodized film density is on the high side, improving abrasion resistance and corrosion  
10 resistance for the film.

11 [0056] Test coupons of the LP™ alloy with protective aluminum oxide film were  
12 prepared and tested for corrosion resistance of the structure. Film corrosion resistance  
13 was tested using a "hydrogen bubble test". In particular, the purpose of the test was to  
14 infer the integrity of an anodized film by measuring the time before the film is breached  
15 by hydrochloric acid applied to the film surface. The test could be made using  
16 hydrofluoric acid, but the state of California will not permit the use of this substance as a  
17 test reagent, so it was not used herein. The hydrochloric acid used in the test was a 5%  
18 by weight concentration. A rigid, transparent polymer or glass tubing section having a  
19 diameter of about 0.5 to about 1.5 inch, and a length of at least one inch, with ends cut  
20 flush, was sealed to the upper surface of the anodized film on the test coupon. The seal  
21 must be water proof and acid proof and was created in this instance using an o-ring and  
22 clamps. The test coupon, hydrochloric acid solution and ambient temperature was  
23 between 20 °C and 30 °C during testing. The test coupon was mounted so that the test  
24 surface was horizontal and facing upward. No portion of the anodized surface within the  
25 sealed tubing was within 0.7 inch of the edge of the test coupon. The hydrochloric acid  
26 solution was introduced into the tubing to a depth of at least 0.6 inches, and a timer was  
27 started or the time was noted. After a minimum specified time had elapsed, the test

1 coupon was observed for the presence of a stream of bubbles rising from the anodized  
2 film surface. Hydrochloric acid reacts with aluminum oxide with little gas generation;  
3 however, hydrochloric acid produces a noticeable amount of hydrogen gas when reacting  
4 with the aluminum alloy. Failure of the aluminum oxide film to protect the underlying  
5 aluminum alloy is clearly indicated by the bubbles rising from the film surface. Testing  
6 was continued until bubble formation was observed. After completion of the test, the  
7 residual hydrochloric acid was removed, and the test coupon with sealed tubing applied  
8 was flushed with ionized water at least twice. The tubing was then removed and the  
9 surface of the anodized protective film was wiped with deionized water and then with  
10 isopropyl alcohol. The film surface could then be further inspected if desired.

11 [0057] Test data for a 6061 aluminum alloy protected by a standard anodized  
12 coating about 25  $\mu\text{m}$  thick shows hydrogen bubble test failure after about 2 hours of  
13 exposure on the average. Test data for the LP<sup>TM</sup> aluminum alloy protected by an  
14 anodized film prepared by the method of invention described herein shows bubble test  
15 failure only after at least 20 hours of exposure.

16 [0058] The above described exemplary embodiments are not intended to limit the  
17 scope of the present invention, as one skilled in the art can, in view of the present  
18 disclosure, expand such embodiments to correspond with the subject matter of the  
19 invention claimed below.